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(21) International Application Number: PCT/GB99/03312 (22) International Filing Date: 7 October 1999 (07.10.99) (30) Priority Data: 9822056.9 10 October 1998 (10.10.98) GB (71)(72) Applicants and Inventors: BRATTON, Graham, John [GB/GB]; 30 Cavendish Avenue, Sidcup, Kent DA15 9EB (GB). NAYLOR, Timothy, De Villiers [GB/GB]; Englefield Green, Surrey TW2 0NQ (GB). BUCK, Karon, Doreen [GB/GB]; Alancroft, Kingsfield Road, West Kingsdown, Kent TN15 6LH (GB). MAJOR, Martin, Grayling [GB/GB]; 32 Orchard Road, Welling, Kent DA16 1QG (GB). (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MEMBRANE PRE-TREATMENT PROCESS		
(57) Abstract An improved porous substrate for zeolite membranes is formed by coating the substrate with a layer of zeolite particles of a narrow particle distribution size of between 20 and 0.01 microns.		

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Membrane Pre-Treatment Process

The present invention relates to a method for forming inorganic membranes, more particularly it relates to a method for forming zeolite membranes.

5

It is known to form zeolite membranes by crystallisation of zeolites from gel solution onto a substrate such as a metal mesh substrate or a porous ceramic substrate. The membranes which can be used in the present invention can be formed by any method, for example by crystallisation from a gel or solution, by plasma deposition or by any
10 other method such as electro-deposition of crystals on conducting substrates e.g. as described in DE 4109037.

When the membrane comprising a film of zeo-type material is prepared by crystallisation from a synthesis gel, any of the methods described in the prior art can
15 be used for example, as described in EP-A-57049, EP-A-104800, EP-A-2899 and EP-A-2900. Standard text books by D W Breck ("Zeolites Molecular Sieves, Structure Chemistry and Use") published by John Wiley (1974) and P.A Jacobs and J.A Martens (Studies in Surface Science and Catalysis No. 33, Synthesis of High Silica Alumino silicate Zeolites" published by Elsevier (1987), describe many such
20 synthesis gels. The process which can be used includes conventional syntheses of zeo-type materials, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat.

Preferred methods are disclosed in our copending patent applications
25 PCT/GB96/00243, PCT/GB97/00928 and PCT/GB 97/00635.

It is known to pre-treat the substrate before deposition of the zeolite onto the mesh e.g. as described in patent application US 5,716,527.

We have now discovered a method of pre-treating a porous substrate to give an improved membrane.

5 According to the invention there is provided a method of treating a porous substrate which method comprises passing a suspension of zeolite particles in a liquid suspension through the porous support until a coating of zeolite particles is formed on the support surface and in which the particles have a diameter of between 20 μ m and 0.1 μ m.

10 We have found that a narrow size range of zeolite particles gives unexpectedly superior results.

15 Preferably the range of particles is achieved by mixing together particles of different size distribution. Zeolite particles, when prepared will have a particle size distribution, if these particles are ground or pulverised the average size is reduced and the distribution of sizes changed. If these particles are mixed with the unground particles a mixture can be obtained with a preferred size distribution for use in the present invention.

20 Preferably the zeolite particles are a mixture of particles which conforms approximately to a modified Fuller curve.

25 Fuller curves are grading curves which give the minimum void space and closest packing for sands and other mineral aggregates containing particles of varying sizes. The shape of the Fuller curve will depend on the maximum particle size, but will be a single curve for any given maximum particle size.

30 The Fuller curves are described in a paper by Fuller and Thomson entitled "The laws of Proportioning Concrete" published in the Transactions of the American Society of Civil Engineers, 1907, 59, pages 67-172. The Fuller curves are identified by their

maximum particle size. e.g. in the present invention a preferred particle distribution is a 20µm Fuller curve.

5 The porous supports on which zeo-type membranes are formed and which can be used in the present invention include those formed of metals, ceramics, glass, mineral, carbon or polymer fibres or cellulosic or organic or inorganic polymers. Suitable metals include titanium, chromium and alloys such as those sold under the Trade Marks "Fecralloy" and "Hastalloy" and stainless steels. The porous supports may be formed of a mesh or from sintered metal particles or a mixture of both. These are
10 commonly sold in the form of filters.

Porous ceramics such as glass mineral or carbon materials are preferred including alumina, porous silicon and other carbides, clays and other silicates and porous silica. If desired, the support can be a zeolite formed by compression or using a binder. The
15 shape of the support is not critical. for example. flat sheet, tubular, wound spiral, etc. can be used.

The porous support can be also be a granular solid e.g. formed of particles of a closely packed material such as a pellitised catalyst.

20

The present invention can be used with porous supports of any suitable size although, for large flux rates through a membrane, large pore sizes are preferred. Preferably pore sizes of 0.01 to 2,000 microns, more preferably of 0.1 to 200 and ideally of 0.1 to 20 microns are used. Pore sizes up to 300 microns can be determined by bubble point
25 pressure as specified in ISO 4003. Larger pore sizes can be measured by microscopic methods.

The method of the present invention is particularly useful for forming a zeolite membrane on the inside of a tubular porous support e.g. in a ceramic monolith.

30

In this application of the method of the invention a suspension of the zeolite particles is passed through the bore of the tube and out through the walls of the tube so as to deposit a layer of zeolite membranes on the inner surface of the tube.

- 5 The process is continued until the desired thickness of particles are deposited on the inner surface or a pre-determined flux of the liquid passes through the tube walls.

10 The suspension of zeolite particles is preferably an aqueous suspension of the particles and the suspension can be formed by forming a mixture of zeolite particles and water and grinding this mixture in a grinder until the particles are of the requisite size for use in the invention. The particles can be ground or milled in a conventional grinder or mill. Alternatively the particles can be reduced in size by a combination of shear, cavitation and impact e.g. as occurs in a microniser. These ground particles can be mixed with particles of a larger size so that the required particle size distribution is
15 obtained.

After treatment a zeolite membrane can be formed on the treated substrate by any of the methods described in the prior art referred to above and the method is particularly useful when the membrane is formed by gel crystallisation.

20

The invention is described in the following example

Example

- 25 The apparatus shown in Figure 1 was used to deposit the zeolite particles, this apparatus consists of a reservoir vessel (3) connected via a circulating pump (2) capable of achieving flow rates of 16 l/min and a pressure of 35 psi. to the tubular membrane (8) which is held in an appropriate housing (1). The feed outlet is connected back to the reservoir vessel via a pressure gauge (4) and an adjustable
30 valve (5) capable of totally restricting the feed flow. The permeate outlet (7) from the

housing is also connected to the reservoir vessel via flexible tubing that allows samples of permeate flow to be taken over timed intervals. The temperature is monitored by temperature gauge (6).

- 5 The following method is used to deposit the zeolite crystals.

To 7 litres of distilled, deionised water are added 30g of standard zeolite 4A particles having an overall particle size distribution between 20 μm and 0.1 μm as shown in Figure 2 and 3g of zeolite 4A particles that have been micronised to an overall size range between 20 and 0.1 μm , as shown in Figure 3 as measured by a Fritsch Particle Size Analyser Model 22. The particle distribution before micronisation is shown in Table 1 and the particle distribution after micronisation is shown in Table 2 respectively.

15

Table 1 Particle size before micronisation (volume %)

	00.50 %	< 0.20 μm	00.90 %	< 0.24 μm
	03.32 %	< 0.43 μm	04.30 %	< 0.49 μm
20	05.00 %	< 0.53 μm	10.00 %	< 0.77 μm
	15.00 %	< 1.02 μm	20.00 %	< 1.33 μm
	30.00 %	< 2.16 μm	40.00 %	< 3.15 μm
	50.00 %	< 4.05 μm	60.00 %	< 4.88 μm
	70.00 %	< 5.75 μm	80.00 %	< 6.75 μm
25	90.00 %	< 8.29 μm	99.00 %	< 12.62 μm

Table 2 Particle Size after micronisation (volume %)**Interpolation Values**

	00.50 %	< 0.17 μm	00.90 %	< 0.19 μm
	03.32 %	< 0.30 μm	04.30 %	< 0.34 μm
5	05.00 %	< 0.37 μm	10.00 %	< 0.53 μm
	15.00 %	< 0.66 μm	20.00 %	< 0.79 μm
	30.00 %	< 1.05 μm	40.00 %	< 1.35 μm
	50.00 %	< 1.69 μm	60.00 %	< 2.05 μm
	70.00 %	< 2.47 μm	80.00 %	< 2.97 μm
10	90.00 %	< 3.69 μm	99.00 %	< 5.64 m

This suspension is circulated around the system under crossflow conditions for 1 minute (valve (5) fully open). Permeate is collected after this time for 30 seconds and weighed prior to returning it to the main reservoir. Valve (5) is fully closed for 1 minute to ensure all the flow passes through the walls of the porous support. Again the permeate is collected for 30 seconds, weighed and returned to the reservoir valve (5) is then fully opened for 1 minute.

This procedure of opening and closing the valve (5) is continued until the target flux through the porous medium is reached. For example for an alpha alumina porous substrate with a pore size range between 4.5 and 1.3, the target permeate flux is < 50 cm^3 per minute in dead end flow conditions.

The tube is removed from the apparatus, allowed to dry at 70°C for 3-4 hours

25

The zeolite membrane was formed on the inside of the support pre-treated with the particles by allowing a hydrogel suspension to be in contact with the surfaces under the conditions described below.

The hydrogel is formed by combining two separate solutions, (solution A) and (solution B) to form a homogeneous suspension.

Solution A

5

24.49g Sodium Aluminate, 3.75g Sodium Hydroxide and 179.74g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48% Al_2O_3 , 35.24% Na_2O , and 2.28% H_2O .

10 Solution B

50.57g Sodium Silicate of composition 14.21% Na_2O , 35.59% SiO_2 and 50.20% H_2O was dissolved in 148.8g de-ionised water.

15 Solution A was heated to 50°C and added slowly to solution B which had been pre-heated to 90°C with stirring to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). The mixture was then heated to 95°C . This resulted in a hydrogel having a molar composition

20 2.01 Na_2O : Al_2O_3 : 2.0 SiO_2 : 143.10 H_2O

The pre-treated tube was wetted by immersing it in deionised water for 15 seconds. The tube was then suspended vertically above the bottom of the growth vessel. Hot hydrogel was then added to the growth vessel, care being taken to ensure that all the
25 air was expelled from the inside of the support.

The growth vessel was sealed and heated to 100°C for 5 hours.

After 5 hours the tube was removed from the growth vessel, allowed to cool slightly and then removed and washed clean using deionised water over a period of 16 hours. The ceramic tube was then dried at 100°C for 6 hours.

5 X-ray Analysis showed this to be a Zeolite 4A.

A mixture of polysilicic acids of mean molecular weight of about 800 was diluted with ethanol to 5% wt. solids. 500ml. of this solution was circulated over the feed side of the membrane and drawn through the membrane to treat the surface whilst
10 being heated to 70° C., with vacuum for 5 hours to cross-link the silicic acid in the pores of the membrane.

The tubes were pre-treated with various particles and a zeolite membrane formed on the inner surface of the coated tubes as described above and the results described
15 below.

In run 1 the pre-treatment used the mixture of particles formed as described in Example 1, with properties as described in Tables 1 and 2 above, followed by one zeolite growth.
20

In run 2 the pre-treatment used particles of Table 1 only followed by two zeolite crystal growths.

When only micronised particles of Table 2 were used it was not possible to form a
25 vacuum.

The results for Runs 1 and 2 are shown below in Table 3.

Table 3

	<u>Run 1</u>	<u>Run2</u>
5		
Tube weight clean (grms)	298.43	298.83
Tube vacuum (mbar)	0.786	0.7895
Tube weight after pre-treatment (grms)	298.47	307.69
Increase in weight (grms)	0.04	8.86
10 Tube vacuum after pre-treatment	0.7202	0.69
Weight after crystal growth	299.79	304.14
Increase in weight	1.36	- 3.55
Tube vacuum after growth	0.0088	0.2144

15 **2nd Growth**

Weight after crystal growth	305.76
Increase in weight	1.62
Tube vacuum after growth	0.045

20

The flux characteristics for Run 1 are shown in Fig 4 and the flux characteristics for Run 2 are shown in Table 5.

The performance of the membrane formed in Run 1 are given below in Table 4

25

- 10 -

Table 4

	Feed	Permeate	Total Flux	Water Flux	Water Flux	Solvent Flux	Time
5	%/w/w	% w/w	g/h	g/h	kg/m ² /d	kg/m ² /d	hrs.
	3.32	99.17	34.438	34.152	17.59	0.15	0.5
	1.75	96.9	21.778	21.103	10.87	0.35	0.5
	0.91	88.15	10.258	9.042	4.66	0.63	0.5
	0.44	68.61	8.196	5.623	2.90	1.32	0.6

10

Table 5

	Feed	Permeate	Total Flux	Water Flux	Water Flux	Solvent Flux	Time	Cum. Time
	%/w/w	% w/w	g/h	g/h	kg/m ² /d	kg/m ² /d	hrs.	hrs.
				0.000	0.00	0.00	0.0	0.0
15	3.99	99.34	31.640	31.431	15.62	0.10	0.5	0.5
	2.55	98.48	22.32	21.894	10.88	0.17	0.5	1.0
	1.55	94.23	14.618	13.775	6.85	0.42	0.5	1.5
	0.94	83.74	9.760	8.173	4.06	0.79	0.5	2.0
	0.58	62.68	7.668	4.730	2.35	1.46	0.5	2.5
20	0.36	35.08	7.390	2.592	1.29	2.38	0.5	3.0

As can be seen the mixture of particles of a range of sizes gives superior results.

25

Claims

1. A method of treating a porous substrate which method comprises passing a suspension of zeolite particles in a liquid suspension through the porous support until
5 a coating of zeolite particles is formed on the support surface and in which the particles have a diameter of between 20 μ m and 0.1 μ m.
2. A method as claimed in claim 1 in which the zeolite particles have a range of sizes and are formed by mixing together particles of different size distribution.
10
3. A method as claimed in claim 2 in which ground zeolite particles are pulverised and are mixed with the unground particles.
4. A method as claimed in claim 1 or 2 in which the zeolite particles are a mixture of
15 particles which conforms approximately to a modified Fuller curve.
5. A method as claimed in any one of claims 1 to 4 in which the porous substrate is formed of a metal, ceramic, glass, mineral, carbon or polymer fibres or cellulosic or organic or inorganic polymers.
20
6. A method as claimed in claim 5 in which the porous substrate is formed of a mesh or from sintered metal particles or a mixture of both.
7. A method as claimed in claim 4 in which the porous substrate is an alumina,
25 carbide, clay, silicate, silicon carbide or a porous silica.
8. A method as claimed in claim 6 in which the porous substrate is a granular solid formed of particles of a closely packed material.
- 30 9. A method as claimed in any one of the preceding claims in which the porous

support has a pore size of 0.01 to 2,000 microns.

10. A method as claimed in any one of the preceding claims in which the porous support has a pore size of 0.1 to 20 microns.

5

11. A method as claimed in any one of the preceding claims in which the porous substrate has tubular conduits formed within it and a suspension of the zeolite particles is passed down through the tubular conduits and out through the walls of the tubular conduits so as to deposit a layer of zeolite particles on the inner surface of the tubular conduits.

10

12. A method as claimed in claim 11 in which the suspension of zeolite particles is formed by forming a mixture of zeolite particles and water and grinding this mixture in a grinder until the particles are of the requisite size.

15

13. A porous substrate having a coating of zeolite particles formed on it by the method of any one of claims 1 to 12.

14. A porous substrate as claimed in claim 13 in which there is a zeolite membrane formed on the substrate.

20

15. A porous substrate as claimed in claim 14 in which the membrane is formed by gel crystallisation.

16. A porous substrate formed from a ceramic monolith in which there are tubular conduits formed on the inside of the ceramic monolith and in which there is a coating of zeolite particles formed on the inside walls of the tubular conduits according to the method of any one of claims 1 to 12 and in which a zeolite membrane is formed on the coated walls.

30

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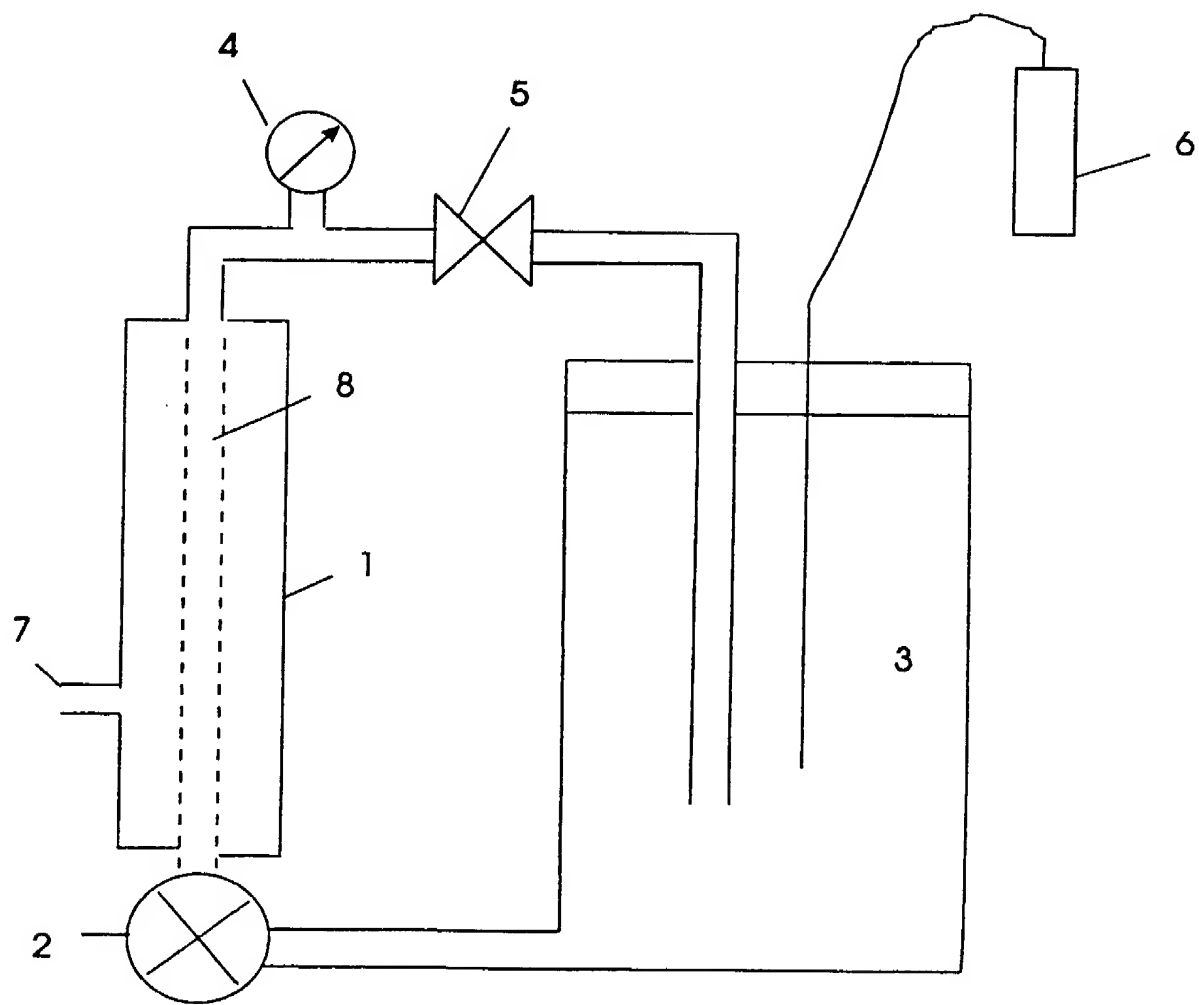


Fig. 1

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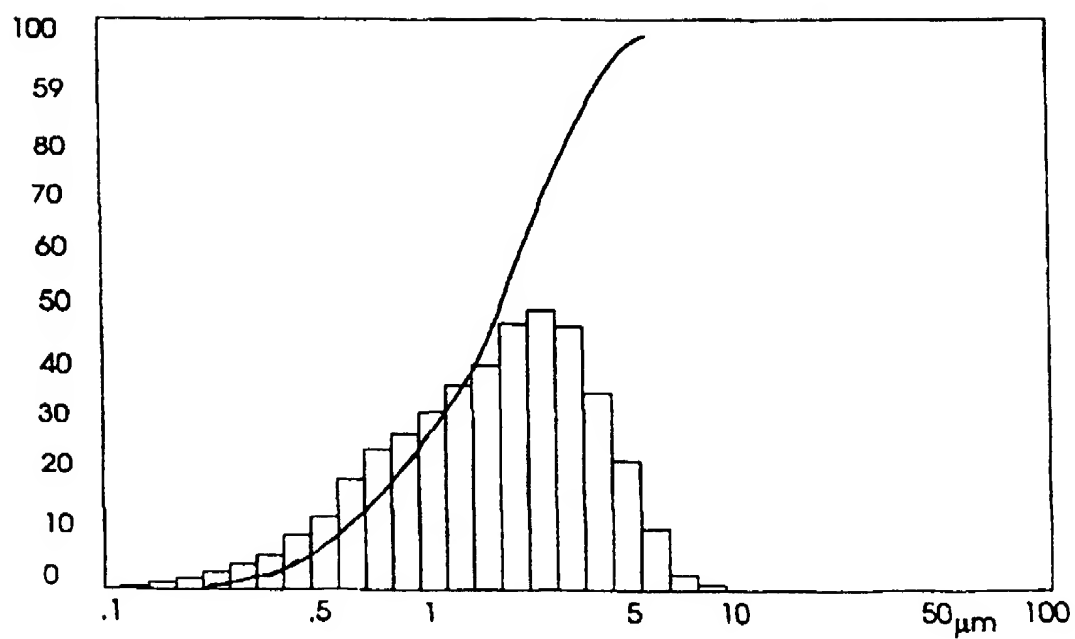


Fig. 2

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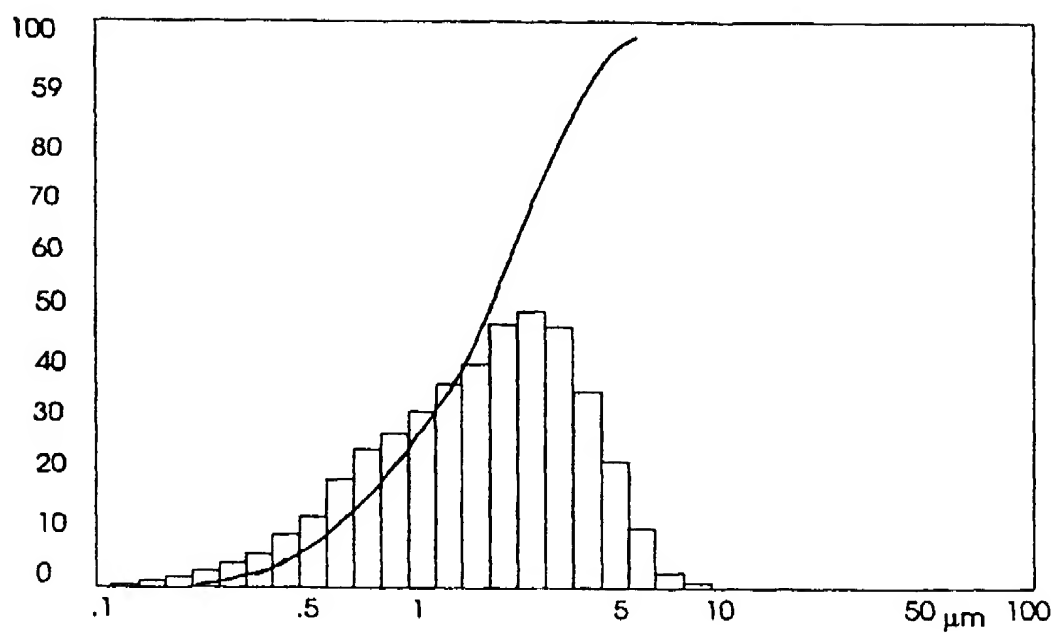


Fig. 3

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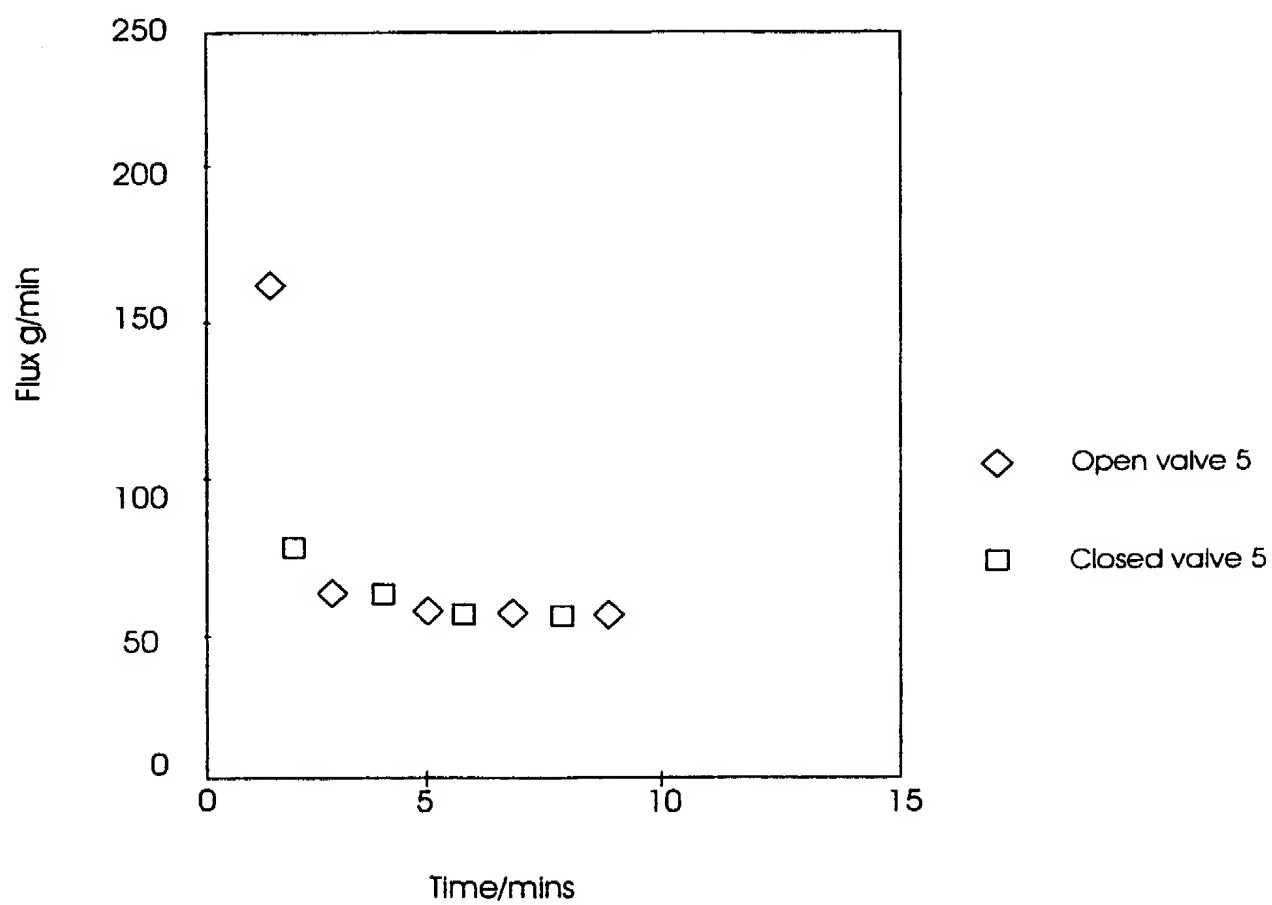


Fig. 4

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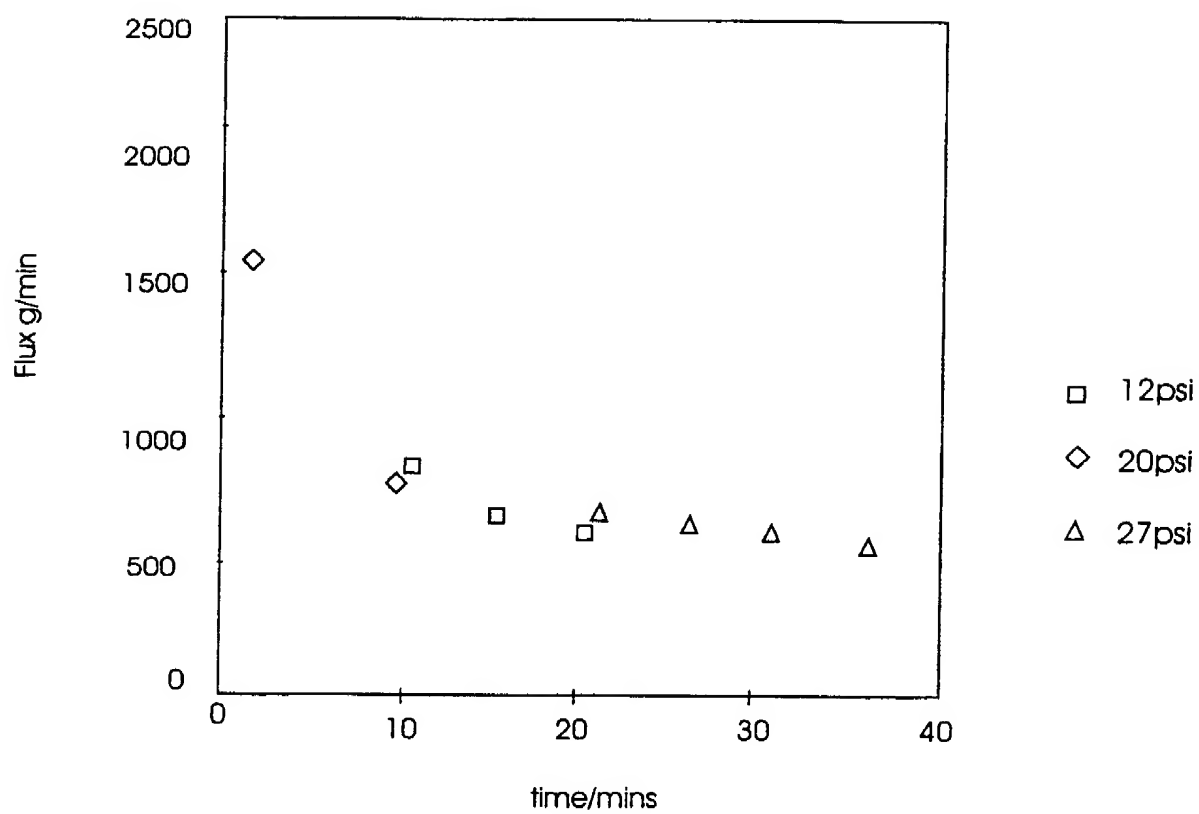


Fig. 5

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D71/02 B01J37/02 B01D63/06

According to International Patent Classification (IPC) or to both national classification and IPC

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IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 468 699 A (FEHLNER JAMES R ET AL) 21 November 1995 (1995-11-21) abstract column 5, line 45 - line 63 example 1	1,5,7,9, 10,13
Y	----	11
X	EP 0 500 154 A (GEN MOTORS CORP) 26 August 1992 (1992-08-26) abstract; claims 1,2,5-7 page 3, line 5 - line 57 page 5, line 14 - line 36 page 8, line 56 -page 9, line 2	1,2,5-8, 13
A	----	12
X	EP 0 466 396 A (ATOMIC ENERGY OF CANADA LTD) 15 January 1992 (1992-01-15) example 1	1,5,6,13
	----- -/-	



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Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 407 880 A (IKEDA TAKUYA ET AL) 18 April 1995 (1995-04-18) abstract; example 1 column 3, line 36 - line 39	1,5,7,13
A	---	12
X	WO 96 09110 A (BRATTON GRAHAM JOHN ;BUCK KARON DOREEN (GB); VILLIERS NAYLOR TIMOT) 28 March 1996 (1996-03-28) claims 1-5,8,10-12 page 3, line 1 - line 19 page 5, line 23 -page 6, line 5 examples 15,19	1,5-10, 13-15
Y	---	16
Y	EP 0 659 469 A (MITSUI SHIPBUILDING ENG) 28 June 1995 (1995-06-28) abstract; claims page 2, line 51 -page 3, line 36 example 1	16
A	---	16
Y	WO 93 19840 A (BRITISH PETROLEUM CO PLC ;BRATTON GRAHAM JOHN (GB); NAYLOR TIMOTHY) 14 October 1993 (1993-10-14) example 1	16
Y	---	11
	US 5 114 581 A (GOLDSMITH ROBERT L ET AL) 19 May 1992 (1992-05-19) abstract column 5, line 36 - line 44 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/03312

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5468699 A	21-11-1995	US 5712461 A	27-01-1998
EP 0500154 A	26-08-1992	US 5114901 A	19-05-1992
		CA 2055756 A,C	20-08-1992
		DE 69203881 D	14-09-1995
		DE 69203881 T	07-12-1995
		JP 5084443 A	06-04-1993
EP 0466396 A	15-01-1992	CA 2020482 A	06-01-1992
		DE 69118258 D	02-05-1996
		DE 69118258 T	22-08-1996
		IE 62999 B	08-03-1995
		US 5157005 A	20-10-1992
US 5407880 A	18-04-1995	JP 6142519 A	24-05-1994
		JP 6198164 A	19-07-1994
WO 9609110 A	28-03-1996	AU 697188 B	01-10-1998
		AU 3526195 A	09-04-1996
		CA 2198128 A	28-03-1996
		EP 0782473 A	09-07-1997
		JP 10507155 T	14-07-1998
		US 5935440 A	10-08-1999
EP 0659469 A	28-06-1995	JP 7185275 A	25-07-1995
		US 5554286 A	10-09-1996
WO 9319840 A	14-10-1993	AU 663181 B	28-09-1995
		AU 3894493 A	08-11-1993
		EP 0632743 A	11-01-1995
		JP 7505331 T	15-06-1995
US 5114581 A	19-05-1992	AT 144162 T	15-11-1996
		AU 655957 B	19-01-1995
		AU 9123091 A	17-08-1992
		CA 2100255 A	11-07-1992
		DE 69122774 D	21-11-1996
		DE 69122774 T	03-07-1997
		EP 0570384 A	24-11-1993
		JP 6506138 T	14-07-1994
		WO 9211921 A	23-07-1992
		US 5221484 A	22-06-1993
		ZA 9110120 A	24-02-1993